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Corrosion from Combustion Products - An Overview

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Corrosion from Combustion Products - An Overview

Abstract

There has been a keen focus to understand corrosion from combustion products as it is related to potential damage from their deposition on equipment. Several test methods are available to assess the potential for corrosion damage from combustion products. These include indirect methods using the pH and conductivity measurements, and also direct methods that measure loss of metal on a target. These are discussed in this presentation. A recent development of determining the reliability of electronic equipment when exposed to combustion products uses an interdigitated target and measures leakage current after the exposure. Data developed using this technique is presented and discussed.

Introduction

There has been a keen focus to understand corrosion from combustion products as it is related to potential damage from their deposition on equipment. Of specific interest is the impact on the reliability of electrical and electronic equipment. Since the effluents can be carried away by the buoyancy of the gases, the potential for damage exists remotely from the fire. For this reason, this phenomenon is also termed "non-thermal fire damage". Another feature of this phenomenon is that in many instances, the damage may become evident after significant passage of time. The time delay for the impact of corrosive deposits to become evident on equipment performance depend upon the rate of chemical reactions taking place, and the availability of the appropriate conditions of temperature and relative humidity.

Three forms of corrosion have been identified. These may be defined as follows:

1. Metal loss due to electrolytic and chemical attack on metal;
2. Leakage current due to increased surface conductance; and
3. Increased contact resistance due to deposition of combustion product and subsequent chemical reactions.

The loss of metal results in reduction in the strength of structural members, and increase in electrical resistance of exposed metal parts. However, the exposed metal components on electronic circuit boards is limited to contacts. The second form of corrosion from the deposition of combustion products on electronic circuit boards, may lead to increased leakage currents to cause malfunction of circuitry. The third form of corrosion influences the electrical resistance between contacts for equipment such as relays and switches. Corrosion between contacts may lead to increased electrical resistance and thus cause a malfunction.

In this paper, the methods currently used to assess corrosion of combustion products, and a new approach to determine the impact of combustion products to the reliability of electronics are presented.

Methods

Several techniques have been devised to determine the corrosiveness of combustion products. These techniques may be divided into indirect measurement, and direct measurement methods.

Indirect Methods of Measurement

The indirect methods of measurement consist of measuring the either halogen acid gases, or the change in pH or electrical conductivity of a solution through which combustion products have been bubbled. Some of the methods have been standardized as shown in Table 1.

Table 1 - Indirect Methods of Measuring Corrosion

Standard	Title	Test Method
IEC 754-1[1]	Test on gases evolved during combustion of materials from cables - Part 1: Determination of amount of halogen acid gases	Sample: 0.5 - 1 g Furnace: Static Temperature: 800° C Air flow: 0.4 - 0.7 l/min. Test duration: 20 min.
IEC 754-2[2]	Test on gases evolved during combustion of materials from cables - Part 2: Determination of degree of acidity of gases evolved during the combustion of materials taken from electric cables by measuring pH and conductivity.	Sample: 1 g Furnace: Static Temperature: 950 °C Air flow: 0.4 - 0.7 l/min Test duration: 30 min.
VDE 0472[3] Part 813	Testing of cables, wires, and flexible cords; corrosivity of combustion gases	Sample: 1 g Furnace: Dynamic (10mm/min.) Temperature: 750-800° C Air flow: 10 l/hr Test duration: 30 min.

[1] IEC 754 -1, Test on gases evolved during combustion of materials from cables - Part 1: Determination of amount of halogen acid gases, International Electrotechnical Commission, Geneva, Switzerland.
[2] IEC 754-2, Test on gases evolved during combustion of materials from cables - Part 2: Determination of degree of acidity of gases evolved during the combustion of materials taken from electric cables by measuring pH and conductivity, International Electrotechnical Commission, Geneva, Switzerland.
[3] VDE 0472, Part 813, Testing of cables, wires, and flexible cords; corrosivity of combustion gases, Deustsche Institut fur Normung e.V., Postfach, 1107, D-1000 Berlin 30, Germany.

Standard	Title	Test Method
MIL-C-24643, section 4.7.25[4]	Acid gas generation	Sample: 0.25 - 0.5 g Furnace: Static Temperature: Ramped to 800° C in 20 min. Air flow: 60 l/hr Test duration: 60 min.

A typical test arrangement for the pH and conductivity based methods is shown in Figure 1.
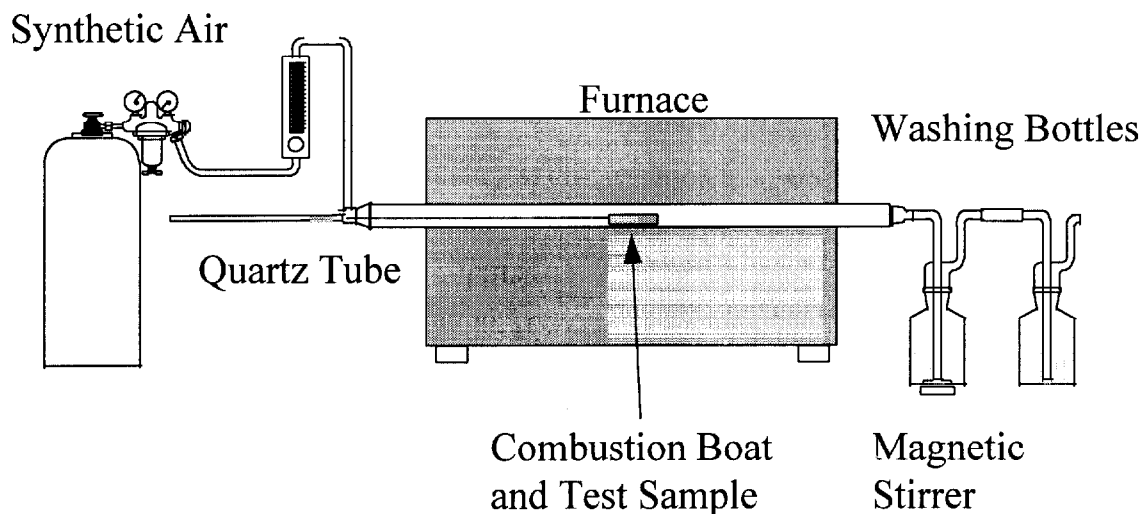

Figure 1 - Typical arrangement of acid gas, pH and conductivity based methods (IEC 754-2)

From Table 1 it may be observed that these methods are material tests. Thus it does not have the ability to determine the influence of finished product construction. IEC 754-2, however, does test the individual materials separately and then provide a weighted average of pH and conductivity of the constituent material of the finished cable. Further, the corrosion potential is inferred from the amount of acid gases (halogen gases), change in pH or electrical conductivity and do not provide a direct measurement the three modes of corrosion.

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[4] MIL-C-24643, section 4.7.25, Acid gas generation, Naval Sea Command, SEA 55Z3, Department of the Navy, Washington DC, 20362.

Direct Measurement Methods

In the US and internationally, some effort has been focused on developing a method that provides a direct measurement of corrosion. In the US, ASTM E-5, and ASTM D-9 considered corrosion methods using metal loss targets. In consideration of the method, several objectives for the test were developed as follows:

- Measure performance
- Ability to test finished product
- Reasonable combustion module
- Possibility of varying combustion conditions
- Reasonable exposure module
- Possibility of varying targets
- Reasonably fast experiments

The last objective may have been identified based on the prolonged post-exposure time to measure loss of metal from coupons exposed to combustion products from shipboard fires[5]. Thus, the need for fast experiments was related to the sensitivity of the measurement technique used.

National Telecommunications laboratory of France (CNET) developed a corrosion test that measured the change in electrical resistance of a printed wiring board. Since the corrosion would reduce the metal loss thickness, the resistance of the target is expected to increase. The test method consists of burning a mixture of 600 mg of test sample, and 100 mg of polyethylene in a 20 liter closed chamber which is initially kept at 50°C. The ignition is accomplished by using an electrically heated coil at a temperature of 800 °C. The combustion products deposit on a water cooled printed wiring board. The temperature of the target is maintained at 40°C during the test. The change in resistance is measured at the end of 1 hour. The test, with some modifications, have now been standardized as ISO 11907-2[6].

A schematic of the target is shown in Figure 2.

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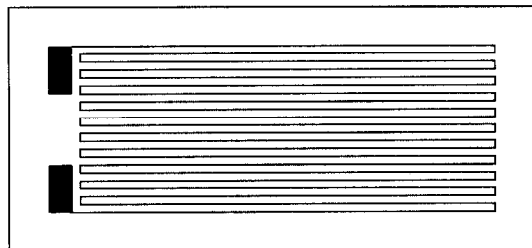
[5] Powell, E.A., Zinn, B. T., "Corrosion of metals exposed to combustion products during shipboard fires, Georgia Institute of Technology, Prepared for Naval Research Laboratory, 1987.
[6] ISO 11907-2 Plastics - Smoke Generation - Determination of the Corrosivity of fire effluents - Part 2: Static Method, International Standards Organization, Case Postale 56, CH-1211, Geneva, Switzerland.

Figure 2 - Schematic of the CNET Electrical Resistance Target

In the US a standard was developed (ASTM D5485[7]) using the Cone Calorimeter radiant heater and exhaust system with the addition of a gas sampling and target exposure system. A schematic of the test apparatus is shown in Figure 3.
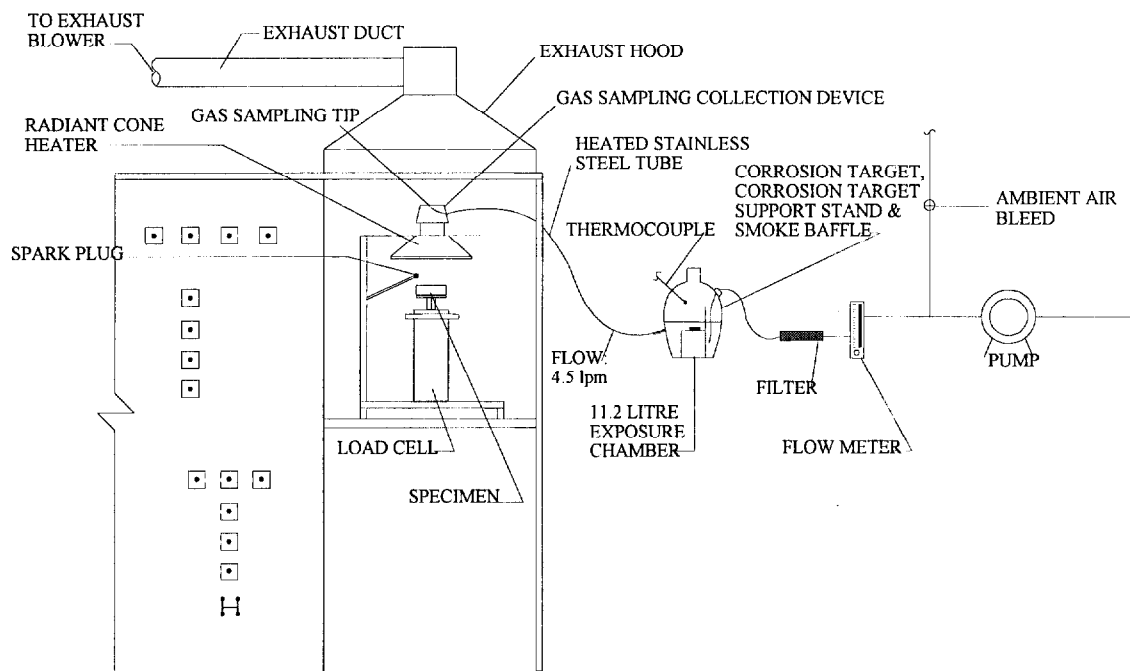
TO EXHAUST BLOWER — EXHAUST DUCT

EXHAUST HOOD

GAS SAMPLING COLLECTION DEVICE

RADIANT CONE HEATER — GAS SAMPLING TIP

HEATED STAINLESS STEEL TUBE

CORROSION TARGET, CORROSION TARGET SUPPORT STAND & SMOKE BAFFLE

AMBIENT AIR BLEED

THERMOCOUPLE

SPARK PLUG

FLOW 4.5 lpm

FILTER

11.2 LITRE EXPOSURE CHAMBER

PUMP

LOAD CELL

FLOW METER

SPECIMEN

H

Figure 3 - Schematic of the ASTM D5485 Test Apparatus

This test uses an electrical resistance target as shown in Figure 4.

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[7] ASTM D5485 - Standard Test Method for Determining the Corrosive Effect of Combustion Products Using a Cone Corrosimeter, American Society for Testing and Materials, 100 Parr Harbor Drive, West Conshohocken, PA, 19428-2959.
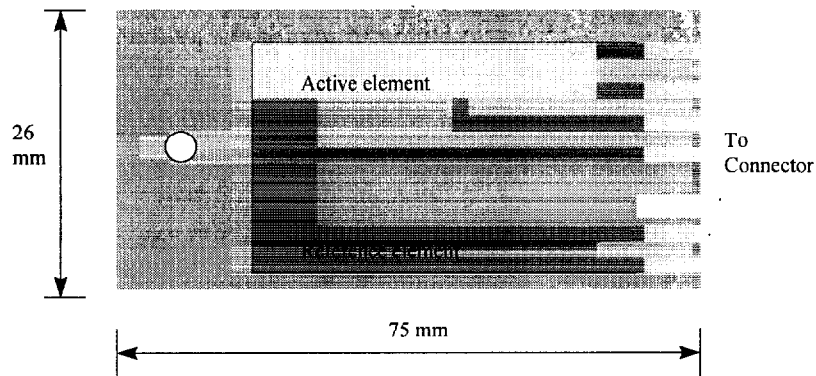
Figure 4 - Schematic of the Electrical Resistance Target for ASTM D5485

This test is conducted in two steps. In the first step, the weight loss characteristics of the sample is determined by conducting two tests at the desired radiant flux level. The corrosion tests are then conducted with the gas sampling until 70% of sample weight loss determined in the first step is attained. The exposure chamber is then sealed, and the target is exposed to the combustion products for a total of 60 minutes. There is an additional 24 hr. post-test exposure at 75% RH, and 75 °F.

Several studies have been conducted to compare the corrosion results obtained from the ISO 11907-2, and the ASTM D5485 test protocols. The data from one of the studies are presented in Figure 5, and Figure 6 respectively[8,9].
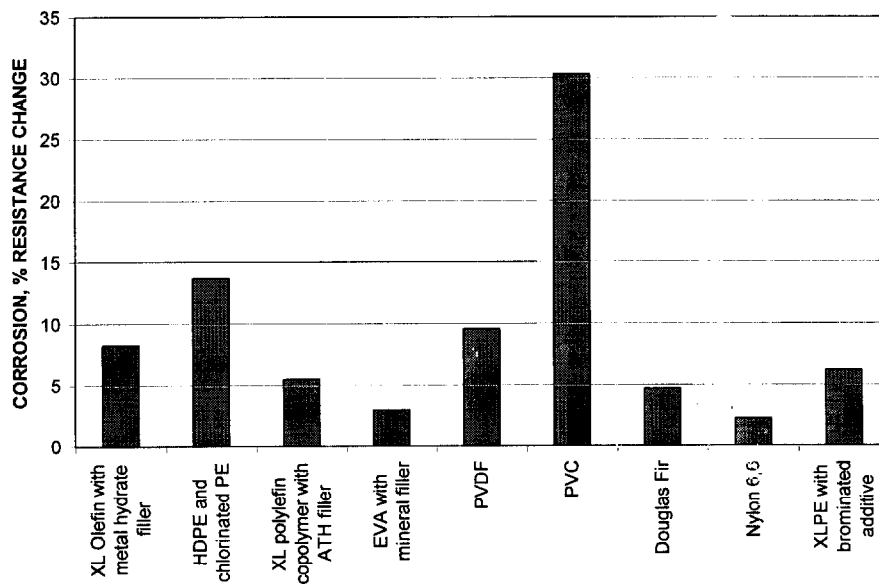

Figure 5 - Results from ISO 11907-2 Test Method (CNET Apparatus)

[8] Rogers C. E., Bennett J. G. Jr., Kessel, S. L., "Corrosivity Test Methods for Polymeric Materials - Part 2 - CNET Test Method," Journal of Fire Sciences, Vol. 12, No. 2, (1994), pp. 134-154.
[9] Bennett, J. G. Jr., Kessel, S. L., Rogers, C. E., "Corrosivity Test Methods for Polymeric Materials Part 4 - Cone Corrosimeter Method," Journal of Fire Sciences, Vol. 12, No. 2, (1994), pp. 175-195.
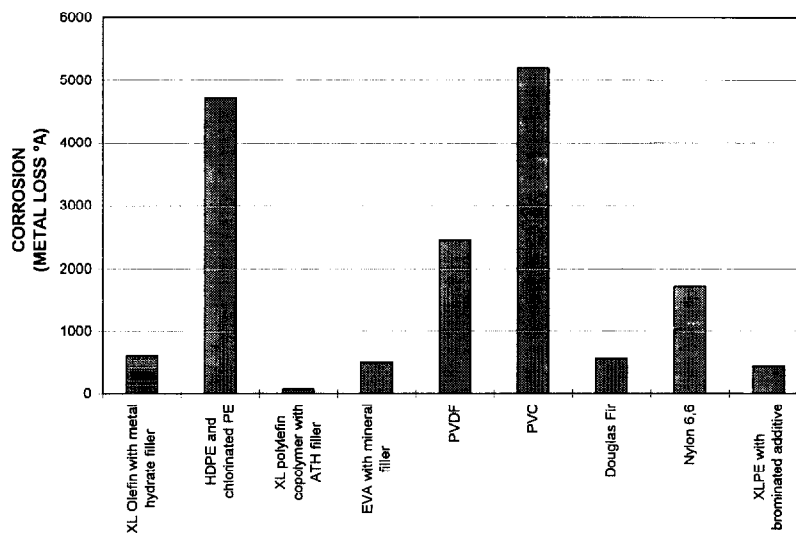
Figure 6 - Results from ASTM D5485 Test Method at 50 kW/m²

It may be observed that a trend is apparent between the data obtained in the CNET and the ASTM D5485 test apparatuses. The CNET test apparatus is a static chamber test. However, the mass of the test sample is small enough that there is more than sufficient oxygen for combustion of the sample[10]. On the other hand, in the ASTM D5485 test, the sample burns under well-ventilated conditions. Figure 7 shows a comparison of the data presented in Figure 5, and Figure 6.
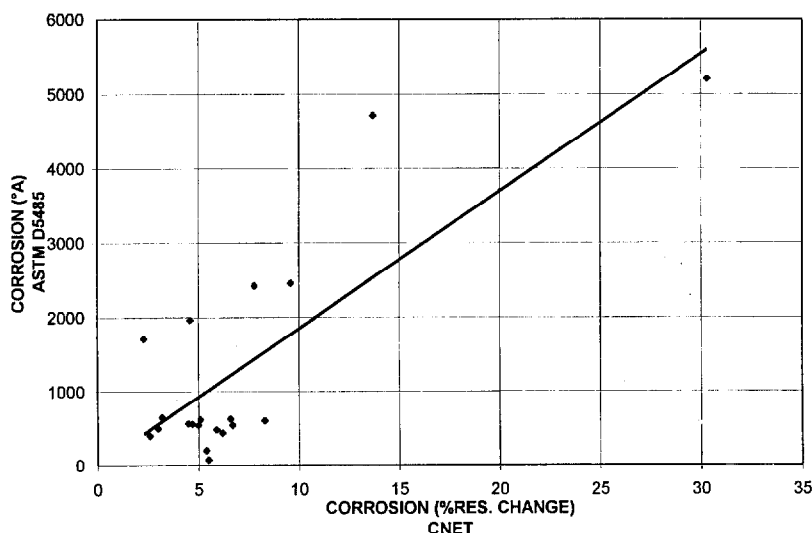

Figure 7 - Comparison of Data from CNET and ASTM D5485 Test Methods

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[10] Gandhi P. D., "Modeling Gas Collection Systems for Corrosion Testing," Fire Safety Journal, Vol. 21, (1993), pp. 47-68.

One of the advantages of the ASTM D5485 method is that it permits testing portions end products such as cable samples. This is important since test items may be manufactured with more than one material and co-combustion of materials constituents can influence the corrosion results. Further, product testing also allows determining the influence of construction. Figure 8 depicts some corrosion data obtained from cable samples using ASTM D5485.
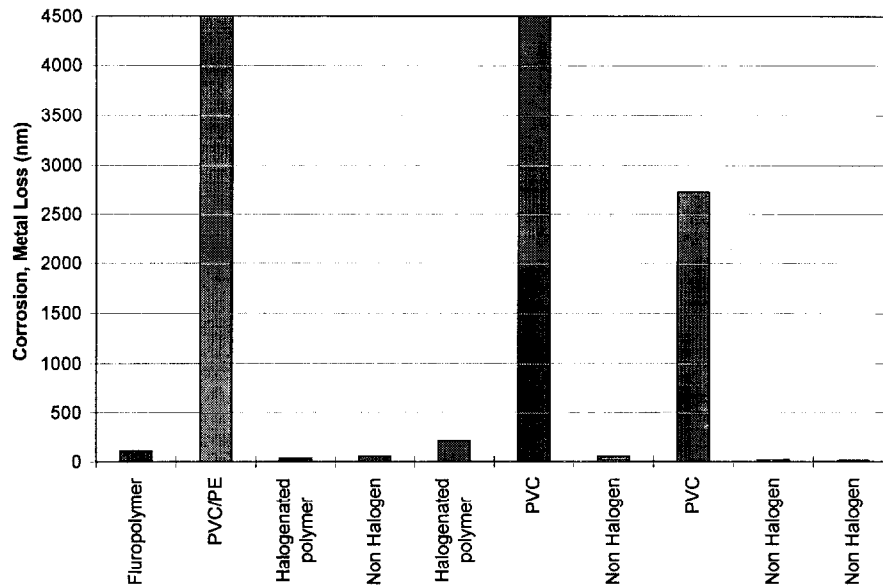

Figure 8 - Results of Corrosion from 4 Pair Communication Cables at 50 kW/m²

Current Leakage

The direct measurement tests that have been developed use metal loss target. This measurement however does not provide information on the impact of deposited combustion products on electronics. In Central Equipment Offices, it has been observed[11] that deposition of dust over a period of time can lead to malfunctio ℩ of circuit boards under appropriate conditions of humidity and temperature. The dust has many ionic substances that cause an increased electrical surface conductance[12]. urther, investigation of this phenomenon has shown that the surface conductance, or leakage current increases with % Relative Humidity. In fact, it has been observed that below a critical humidity level, the leakage current is relatively insignificant. Increase in humidity beyond the critical level results in marked increase in leakage current. Figure 9, adapted from

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[11] Comizzoli, R. B., Frankenthal, P. C., Milner, P. C., Sinclair, J. D., "Corrosion of Electronic Materials and Devices, American Association for the Advancement of Science, Vol. 234, (1986), pp. 340-345.
[12] Sinclair, J. D., Posta-Kelly, L. A., Weschler, C. A., and Shields H. C., "Deposi 'c n of Airborne Sulfate, and Chloride Salts as It Relates to Corrosion of Electronics", Journal of Electroch nical Society, Vol. 137, No. 4, (1990), pp. 1200-1206.

Comizzoli et. al[13], shows the influence of relative humidity on the leakage current from a number of dust samples. It may be noted that below relative humidity of less than 40% the leakage current is negligible, except for dust from the Kuwaiti oil well fires (labeled K10). The high leakage current at low humidity levels for the Kuwaiti samples is suspected to be due to the presence of graphitic carbon resulting from the hydrocarbon fires at the end of the Gulf War.
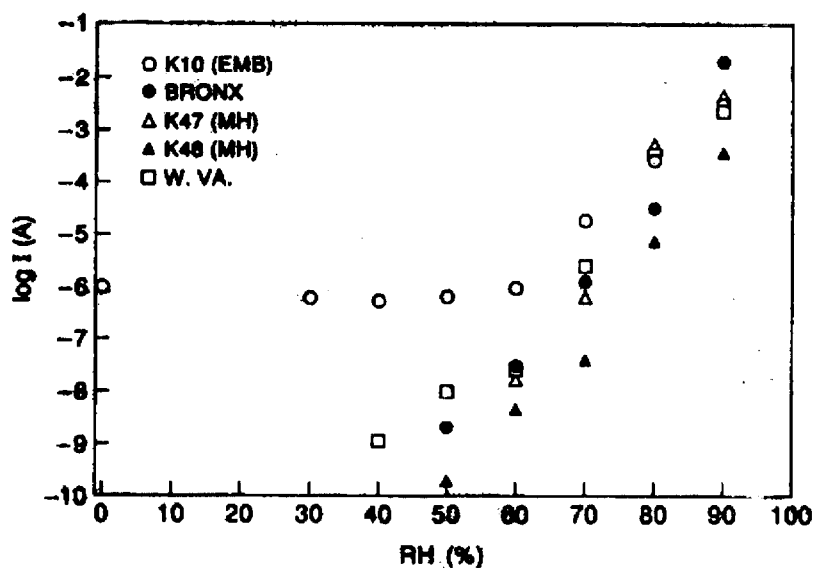

Figure 9 - Influence of Relative Humidity on Leakage Current

Plastics contain fire retardants, fillers, and other additives that may release ionic particles when they are involved in a fire. The thermal plume of a fire then can carry these particles to remote areas where they can deposit on electronic circuitry in a analogous manner to dust particles.

In order to study the influence of combustion products on the leakage current on electronic circuitry, a series of tests were conducted using a tube furnace apparatus similar to that described in IEC 754-2[2].

Leakage Current Experiments

The combustion tube furnace consisted of furnace, silica tube, combustion boat, air supply system, and a mixing chamber for the combustion products. The tube furnace had an inside diameter of 60.3 mm and a heating zone of 300 mm. The test temperature was controlled by an electronic temperature controller. The silica tube was 1600 mm long,

[13] Comizzoli, R. B., Franey, J. P., Kammlot, G. W., Miller, A. E., Muller, A. J., Peins, G. A., Psota-Kelly, L. A., and Wetzel, R. C., "The Kuwait Environment and its Effects on Electronic Materials and Components," Journal of Electrochemical Society, Vol. 139, No. 7, (1992), pp. 2058-2066.

47.5 mm inside diameter and had a wall thickness of 2.75 mm. The silica tube was placed in the tube furnace such that it extended 400 mm from the rear end of the furnace. The rear end of the tube was ground and was fitted with a glass adapter connected to an air supply from a dry compressed air cylinder. A porcelain combustion boat, 97 mm in length, was used to hold the test sample during the test.

The mixing chamber was made from polymethyl methacrylate (PMMA), with dimensions of 310 x 310 x 340 mm. A stainless steel plate was attached to the ner side of part of the chamber connected to the silica tube. The purpose of the plate was to protect the PMMA surface from flames emanating from the silica tube. The top of the mixing chamber was a blowout panel to release excessive pressure. The chamber had a 6.3 mm opening at the bottom of one of the sides to permit exhaust of combustion products to a smoke abatement system. The mixing chamber was placed 385 mm away from the end of the tube furnace, such that 55 mm of the silica tube protruded inside the chamber.

Test Samples

Test samples were obtained commercially. Six materials were used in this investigation. In the combustion tube furnace experiments the IEC 754-2 test specifies a sample weight of 1,000 ± 5 mg. The samples are described in Table 2.

Table 2 - Test Samples

Sample Identification	General Composition
A	Halogenated, flame retardant polyolefin
B	Commercial PVC formulation
C	Non halogenated, flame retardant polyolefin
D	Non flame retardant polyolefin
E	Halogenated, highly flame retarded polyolefin
F	Commercial fluorinated polymer

The samples were conditioned for at least 16 h at a temperature of 23 ± 2 °C, and relative humidity of 50 ± 5 %.

Corrosion Target

The corrosion target consisted of an interdigitated circuit with a spacing between the digits of 12.5 µm. A schematic of the circuit is shown in Figure 10. Prior to testing, the target was cleaned in an ultrasonic bath with 75% isopropyl alcohol, followed by rinsing in de-ionized water for 30 seconds, and drying with compressed nit-ogen.
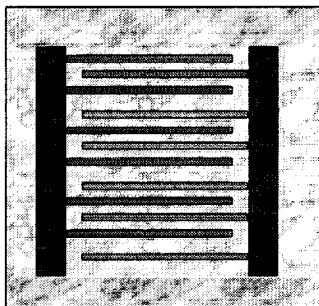

Figure 10 - Schematic of a Interdigitated Corrosion Target

Test Procedure

For each test, the following test procedure was used. The furnace was set at 900 °C. One corrosion target was placed at the bottom and at one of the ends of the mixing chamber as shown in Figure 11. The test samples were weighed to an accuracy of 1 mg and evenly distributed on the bottom of the combustion boat. The test samples with the combustion boat were also weighed. The combustion boat with the test sample were placed inside the rear end of the tube prior to test initiation. The end was closed with the adapter, and an air flow rate of 0.45 liters per minute was established through the silica tube. The combustion products were allowed to react with the corrosion target for 1 hour. At the end of one hour, the target was removed and leakage current characteristics were determined. The combustion boat with residue was weighed and the sample weight loss was determined.
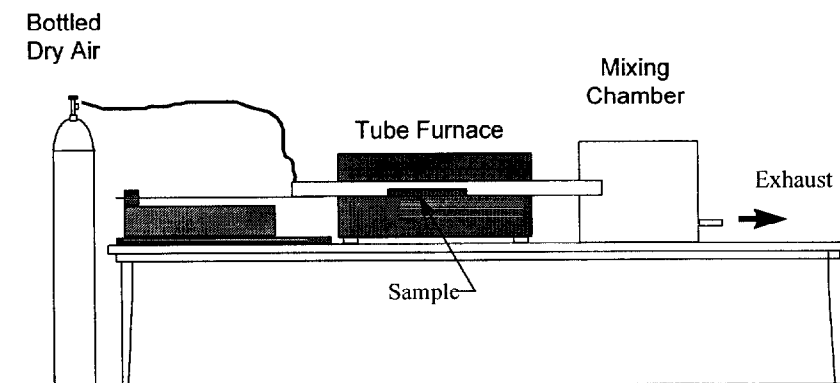
Figure 11 - Leakage Current Test Apparatus

The targets were placed in the controlled RH chamber. A voltage of 5, 50 or 200V was applied. For each voltage, the RH was increased from 30 to 90% and currents were recorded at RH intervals of 5%. Four targets were run as a group.

Results and discussion of Leakage Current Data

The leakage current data for the tube furnace at 5, 50 and 200 volts are presented in Figure 12, Figure 13, and Figure 14.

The leakage current measured on a test pattern is expected to depend not only on the type and quantity of deposited species, but also on the relative humidity (RH), temperature, applied voltage, and the history of the sample including the duration of the RH exposure and voltage application. In light of these factors, the present experiment is a first step demonstration of RH-dependent surface currents after deposition of combusted polymer formulations. Until the effects of RH, time, and voltage are more clearly resolved by the data, a detailed comparison of the polymer formulations may be premature. However, some general observations can be made.

Below about 50% RH, the currents in Figure 12 to Figure 14 are measurable but small, except for Samples B and C. Sample B has significant leakage current, even at 30% RH. At 55% RH Sample B shorted out. Inspection revealed little corrosion, no "growths" of corrosion product, and an apparent smoke "dendrite" bridging two lines. Sample C exhibited unusually large currents at low RH. The current decreased as the RH increased, which is most likely a time effect rather than an RH effect. The current is decaying with time, rather than decreasing because the RH is higher. The current decay is probably related to polarization effects or to formation of corrosion product.

A comparison of current levels at high RH for the three voltages shows that only polymer F has a consistently low current, indicating it is the most benign, at least for these test conditions. Polymer B has a consistently large current, suggesting it may have the most serious smoke effects.

Some of the data shows an approximate exponential dependence of current on RH above about 50% RH. This behavior is typical for surface currents on a wide variety of insulators[11] . This is attributed to the formation of conducting regions between the metal lines. These regions are conducting independent of RH. In some cases microscopic examination revealed bridging structures of presumably conducting smoke. In other cases, charred regions of circuit board material or conducting corrosion product bridges were observed.

Conducting bridges of corrosion product or of smoke particles can usually be disrupted by the passage of sufficient current. Following the disruption, the resistance of the sample increases and lower currents are measured even at higher voltages. The testing

sequence at different voltages is clearly an important variable. For example, sample A had a larger current at 5V than at 50V for the tube furnace exposure.
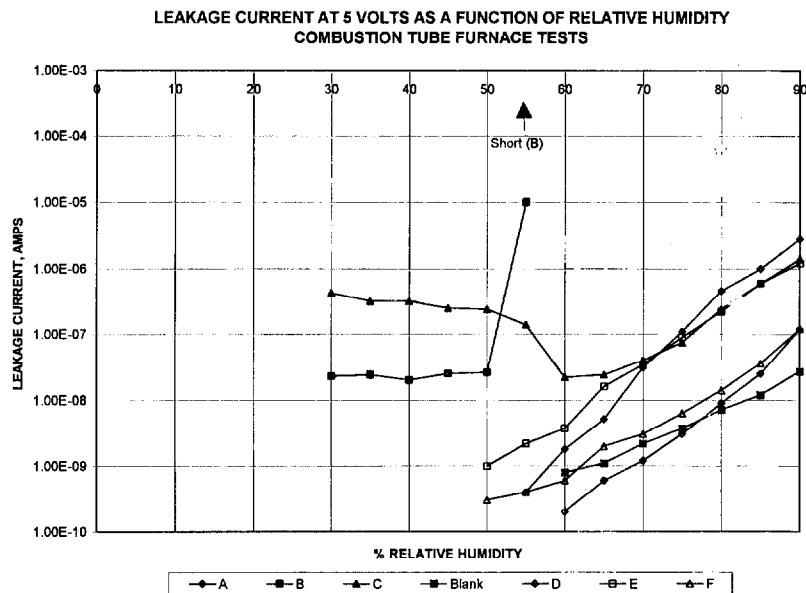
LEAKAGE CURRENT AT 5 VOLTS AS A FUNCTION OF RELATIVE HUMIDITY
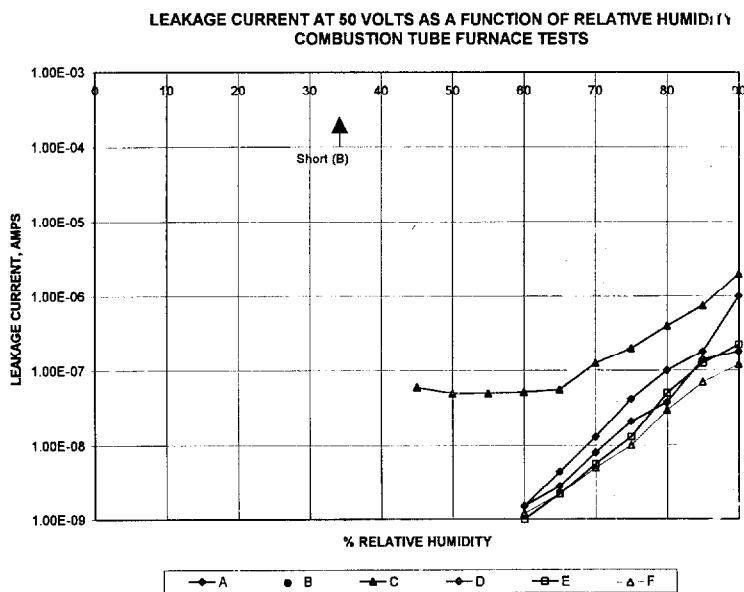COMBUSTION TUBE FURNACE TESTS

Figure 12 - Leakage Current at 5 Volts

LEAKAGE CURRENT AT 50 VOLTS AS A FUNCTION OF RELATIVE HUMIDITY
COMBUSTION TUBE FURNACE TESTS

Figure 13 - Leakage Current at 50 Volts

LEAKAGE CURRENT AT 200 VOLTS AS A FUNCTION OF RELATIVE HUMIDITY
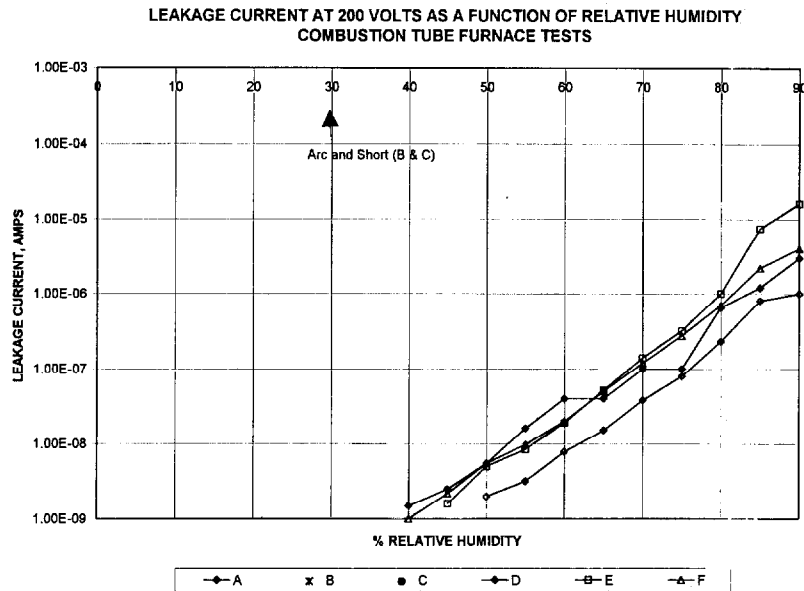COMBUSTION TUBE FURNACE TESTS

Figure 14 - Leakage Current at 200 Volts

Future Work

This study provides information for understanding the smoke corrosivity behavior of
cable jacket and insulation materials. We are anticipating continuing this investigation to
refine the test protocol and correlate to large scale testing. Some areas of future work
include: 1) comparison of data to metal loss behavior, 2) comparison of data to pH and
conductivity data, 3) expanded materials list for testing, 4) conduct SEM/EDAX analysis
of test patterns, 5) analysis of smoke particulate, 6) small and large scale product testing.

Discussion

Patrick Pagni: Which of the two do you think is the more serious problem: condensate on particles or gas phase material as a corrosive agent?

Pravinray Gandhi: In my opinion, the particle condensation is the most problem. This is not based upon any measurements I have made, but is made based upon all the observations I've had in studying the targets after exposition to corrosion particles.